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THIONAPHTHEN DERIVATIVES
FROM
STYRENES AND THIONYL CHLORIDE

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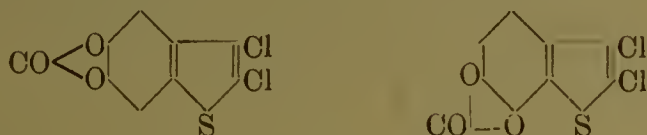
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CCVII.—*The Synthesis of Thionaphthen Derivatives from Styrenes and Thionyl Chloride.*

By GEORGE BARGER and ARTHUR JAMES EWINS.

In an attempt to convert 3 : 4-methylenedioxyphenylmethylecarbinol, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH(OH)\cdot CH}_3$, into the corresponding cyclic carbonate by means of thionyl chloride (compare the preceding paper and Trans., 1908, 93, 563), we found that the reaction proceeds in an unexpected manner; the resulting substance is, indeed, a cyclic carbonate, but it contains sulphur and has the composition $\text{C}_9\text{H}_2\text{O}_3\text{Cl}_2\text{S}$. The same compound was produced when $\alpha\beta$ -dibromo-3 : 4-methylenedioxy-styrene was acted on by thionyl chloride, the bromine being eliminated. Since it contains only two hydrogen atoms, the new substance must possess a condensed ring; it is most probably a thionaphthen derivative, and may be represented by one of the following formulæ :



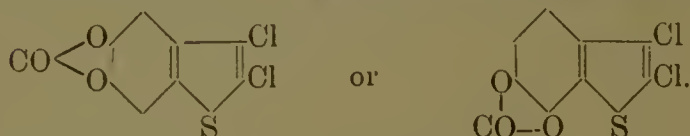
In order to determine whether the reaction is a general one, we submitted derivatives of other styrenes to the action of thionyl chloride. Although organic sulphur derivatives were formed in each case, we were not always able to isolate them from the mixture produced. Thus, from ordinary styrene, we could only obtain a pure substance after we had employed conditions favourable to complete chlorination, the resulting compound being *hexachlorothionaphthen*, $\text{C}_8\text{Cl}_6\text{S}$.

The substances described below do not give the indophenine reaction, but some of them, containing relatively little chlorine, gave, after reduction, a green or bluish-green coloration with isatin and sulphuric acid; the typical blue coloration was never obtained.

In all cases a large excess of thionyl chloride was used, and was heated with the styrene derivative in a sealed tube (to 180—270°). An attempt to carry out the reaction at a low temperature with aluminium chloride and thionyl chloride or sulphur dioxide was unsuccessful. Dibromostyrene was generally employed, not only because it was most readily obtainable, but because it alone was found to yield a crystalline product when the dichloro-derivative did not, even in the presence of iodine. For this superior reactivity of the bromo-compounds we cannot offer an explanation. The yield of pure thionaphthen derivatives was generally small, except in the case of the catechol derivative first investigated, when it amounted to 70 per cent. of the theoretical.

EXPERIMENTAL.

1 : 2-Dichloro-4 : 5(or 5 : 6)-carbonyldioxythionaphthen,



2.2 Grams of 3 : 4-methylenedioxyphenylmethylcarbinol were heated with 13 grams of thionyl chloride for five hours in a sealed tube at 170° . On opening the tube there was found to be a great pressure; the contents were a reddish-brown liquid and a crystalline solid (the thionaphthen). The latter was collected and recrystallised from benzene; the yield was 45 per cent. of the theoretical.

One gram of $\alpha\beta$ -dibromo-3 : 4-methylenedioxy-styrene, heated with 5 grams of thionyl chloride to $250-260^{\circ}$ for seven hours, yielded 0.6 gram of the same substance or 70 per cent. of the theoretical. After repeated crystallisation from benzene, the substance from either source formed white prisms melting at 198° :

0.1668 gave 0.2514 CO_2 and 0.0124 H_2O . $\text{C} = 41.1$; $\text{H} = 0.8$.

0.1151 „ 0.1251 AgCl . $\text{Cl} = 26.9$.

0.2472 „ 0.2150 BaSO_4 . $\text{S} = 11.9$.

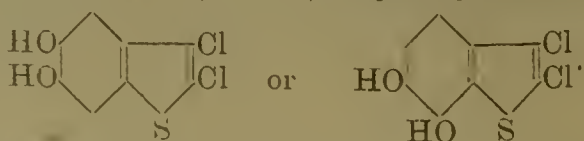
0.3798, in 11.74 naphthalene, gave $\Delta = -0.87^{\circ}$. $\text{M.W.} = 257$.

$\text{C}_9\text{H}_2\text{O}_3\text{Cl}_2\text{S}$ requires $\text{C} = 41.4$; $\text{H} = 0.8$; $\text{Cl} = 27.2$; $\text{S} = 12.2$ per cent.

$\text{M.W.} = 261$.

In addition to the secondary alcohol and the dibromo-derivative already mentioned, the following substances also yielded this thionaphthen derivative on heating with thionyl chloride: the ether, $[\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3:\text{CHMe}]_2\text{O}$; the dichloride, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3:\text{CHCl}:\text{CH}_2\text{Cl}$, and the corresponding chloro- and bromo-hydrins. Since the side-chain in all these cases is readily chlorinated, the chlorine atoms in the resulting thionaphthen derivative are in all probability in positions 1 and 2. The para-hydroxyl group must be in position 5, and the meta-hydroxyl in either 4 or 6; that the substance is a cyclic carbonate is proved below.

1 : 2-Dichloro-4 : 5(or 5 : 6)-dihydroxythionaphthen,



The previously-described substance, $\text{C}_9\text{H}_2\text{O}_3\text{Cl}_2\text{S}$, was hydrolysed by gently warming it in an atmosphere of hydrogen with 50 per cent. aqueous pyridine; carbon dioxide was evolved. The yellow solution

was evaporated in a vacuum over sulphuric acid, the residue was dissolved in water, and the aqueous solution extracted with ether. After washing with dilute sulphuric acid, drying, and evaporating the ethereal solution, the remaining solid was dissolved in hot benzene from which it separated on cooling as a white, gelatinous mass melting and decomposing at 148° :

0.1482 gave 0.1848 AgCl and 0.1448 BaSO₄. Cl = 30.8; S = 13.4.

C₈H₄O₂Cl₂S requires Cl = 30.2; S = 13.6 per cent.

The *dichlorodihydroxythionaphthen* thus prepared is soluble in water and in most organic solvents. Its aqueous solution yields with ferric chloride a bluish-green coloration, differing somewhat from the pure green obtained with simple catechol derivatives.

The *dibenzoyl* derivative was prepared by Einhorn's method, and yielded, on crystallisation from a mixture of alcohol and benzene, long, slender needles melting at 185° :

0.1503 gave 0.0993 AgCl. Cl = 16.3.

C₂₂H₁₂O₄Cl₂S requires Cl = 16.0 per cent.



Two grams of $\alpha\beta$ -dibromostyrene were heated with 5 c.c. of thionyl chloride and 2 c.c. of sulphuryl chloride to 270° for thirteen hours. On cooling, the tube contained a red liquid in which crystals were suspended. The latter were recrystallised from light petroleum (b. p. $70-100^{\circ}$); they formed long, silky, white needles melting at 158° :

0.0959 gave 0.0977 CO₂ and 0.0005 H₂O. C = 27.8; H = 0.06.

0.1640 „ 0.4189 AgCl and 0.1188 BaSO₄. Cl = 63.2; S = 9.9.

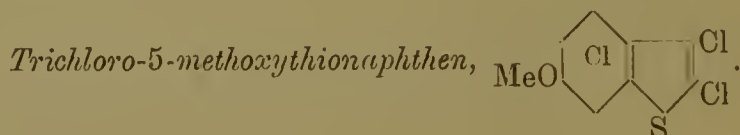
C₈Cl₆S requires C = 28.1; Cl = 62.5; S = 9.4 per cent.

In a previous experiment, when the sulphuryl chloride was omitted and the temperature maintained at $215-240^{\circ}$ for ten hours, the same crystalline hexachlorothionaphthen was obtained, but the analysis showed it to be impure. Subsequently, sulphuryl chloride and a higher temperature were used to ensure complete chlorination.

The (crude) reduction product of hexachlorothionaphthen with hydriodic acid and phosphorus gave a reddish-purple coloration with isatin and sulphuric acid, changing to green on standing.

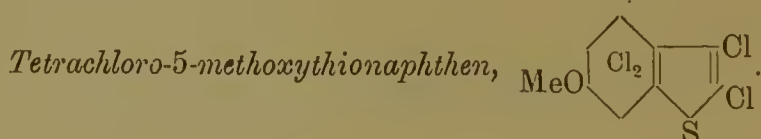
When heated with thionyl chloride to 210° for four to five hours, $\alpha\beta$ -dichlorostyrene furnished a distillate (b. p. $150-175^{\circ}/16$ mm.) containing both chlorine and sulphur, but no crystalline product

could be obtained, nor was any obtainable from phenylmethylecarbinol, even after heating to 240° for twenty hours. The distillate in the latter case gave a brilliant red coloration with isatin and sulphuric acid, and, after distillation with zinc dust, the same reagents produced a green coloration.



By heating 1.5 grams of *p*-methoxyphenylmethylecarbinol (from anisaldehyde) with 12 grams of thionyl chloride for three hours to 200°, and distilling under diminished pressure, a viscid liquid was obtained (b. p. 195—215°/12 mm.), which yielded a small quantity of a substance crystallising from light petroleum in white needles and melting at 153° :

0.0747 gave 0.1152 AgCl and 0.0649 BaSO₄. Cl = 38.2 ; S = 12.1.
C₉H₅OCl₃S requires Cl = 39.8 ; S = 12.0 per cent.



By heating 1.5 grams of *p*-methoxyphenylmethylecarbinol with 12 grams of thionyl chloride to 180° for eight hours, and removal of the excess of thionyl chloride on the water-bath, 3.6 grams of a distillate were collected, b. p. 200—225°/12 mm.

On dissolving in hot light petroleum (b. p. 70—100°) and cooling, 0.35 gram of silky, white needles, m. p. 109—111°, separated.

The melting point was unchanged by recrystallisation :

0.1536 gave 0.2966 AgCl and 0.1265 BaSO₄. Cl = 47.7 ; S = 11.3.
C₉H₄OCl₄S requires Cl = 46.8 ; S = 10.6 per cent.

As the analyses show, neither this nor the previous substance was obtained quite pure ; they are formed simultaneously, and the small quantities at our disposal did not enable us to effect a complete separation. In either case the methoxy-group must be in position 5 ; that of the chlorine atoms in the benzene ring is doubtful.

Action of Thionyl Chloride on isoSafrole Dibromide.

isoSafrole dibromide reacts less readily with thionyl chloride than its lower homologue ($\alpha\beta$ -dibromomethylenedioxy-styrene), but, nevertheless, yielded a small quantity of a thionaphthen derivative. From *isosafrole* dichloride, however, this derivative could not be obtained ;

thus again illustrating the greater reactivity of the bromo-compound as compared with the chloro-compound.

Dichlorocarbonyldioxymethylthionaphthen was obtained by heating 3 grams of *isosafrole* dibromide with 13 grams of thionyl chloride to 220° for seven hours. On opening the tube, a few crystals were found to have separated, and, after cooling to -80°, 0.15 gram was collected. On recrystallisation from light petroleum (b. p. 70—100°), the substance melted at 180° :

0.1012 gave 0.1049 AgCl and 0.0879 BaSO₄. Cl = 25.6 ; S = 11.9.

C₁₀H₄O₃Cl₂S requires Cl = 25.8 ; S = 11.6 per cent.

The constitution is doubtful, but the methyl group is most probably in position 1.

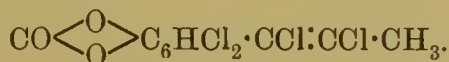
In addition to the above, a substance was obtained, which crystallised from light petroleum, melted at 167°, and did not contain sulphur :

0.1288 gave 0.1793 CO₂ and 0.0115 H₂O. C = 37.9 ; H = 1.0.

0.1689 ,, 0.3097 AgCl. Cl = 45.3.

C₁₀H₄O₃Cl₄ requires C = 38.2 ; H = 1.2 ; Cl = 45.2 per cent.

This substance is most probably represented by the formula



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